



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 18 Oct 2010

To cite this article: M. Aronishidze, A. Chanishvili, G. Chilaya, G. Petriashvili, S. Tavzarashvili, L. Lisetski, I. Gvozдовskyy & I. Terenetskaya (2004): Color Change Effect Based on Provitamin D Phototransformation in Cholesteric Liquid Crystalline Mixtures, *Molecular Crystals and Liquid Crystals*, 420:1, 47-53

To link to this article: <http://dx.doi.org/10.1080/15421400490478353>

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COLOR CHANGE EFFECT BASED ON PROVITAMIN D PHOTOTRANSFORMATION IN CHOLESTERIC LIQUID CRYSTALLINE MIXTURES

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It has been shown that UV radiation can produce observable color changes in induced cholesteric systems (nematic + optically active dopant) additionally doped with ergosterol (provitamin D₂). The effect is based on the photoinduced conversion of ergosterol into vitamin D₃, which has the opposite sign of its helical twisting power. The observed shifts of the selective reflection peaks (more then 100 nm after 10 min of UV irradiation) allow both instrumental and visual monitoring of biologically active UV radiation.

Keywords: induced cholesteric; provitamin D phototransformation; UV monitoring

INTRODUCTION

The cholesteric mesophase is an excellent medium, sensitive to the smallest changes in molecular structure [1,2]. Photo-optical effect in absorbing liquid crystals (LC) have been studied mostly in systems where the chemical structure of conformation of the constituent molecules is changed by irradiation [3,4]. A color shift in induced cholesteric LC systems (mixtures of an achiral LC with an optically active mesomorphic or nonmesomorphic dopant [5–7])

We are thankful to Merck for supplying liquid crystal materials and chiral dopants. The work was supported by the STCU (Project No Gr-50).

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was observed when a conformationally active dye was added to a cholesteric liquid crystal [8], or when a photoisomerizable chiral compound was used as a chiral dopant [9–12]. Recently, the use of a photoisomerizable nematic component in induced cholesteric mixtures has been proposed [13–16].

In this work we continue the realization of a new idea [17,18]: the use of vitamin D derivatives as chiral dopants in induced cholesteric structures. This approach is very promising for a new application of liquid crystals—development of photosensitive cholesteric mixtures controlled by the solar UV radiation and directly representing the vitamin D synthetic capacity of sunlight [17–21].

As is known, vitamin D¹ synthesis consists of the two stages of monomolecular isomerizations (Scheme 1) [22,23]. At the first stage, UV irradiation of provitamin D within its absorption band (240–315 nm) yields previtamin D by hexadiene ring-opening (the C9–C10 chemical bond break in the ring B). Once formed, previtamin D is converted into vitamin D by thermo-induced intramolecular hydrogen shift.

It was found that Provitamin D induce right-handed helical twisting in nematic liquid crystals, while the helix induced by vitamin D is left-handed [24]. Unfortunately, the helical twisting power of compounds from the vitamin D group is too small for induction of a cholesteric structure with helical pitch values, ensuring selective reflection in the visible spectral range² [24]. Therefore, our first idea of liquid-crystalline UV biosensor lay in the use of a wedgelike LC cell filled with the two-component mixture (NLC + provitamin D). In this case the Cano stripes diminishing number is proportional to the accepted UV dose [17–19].

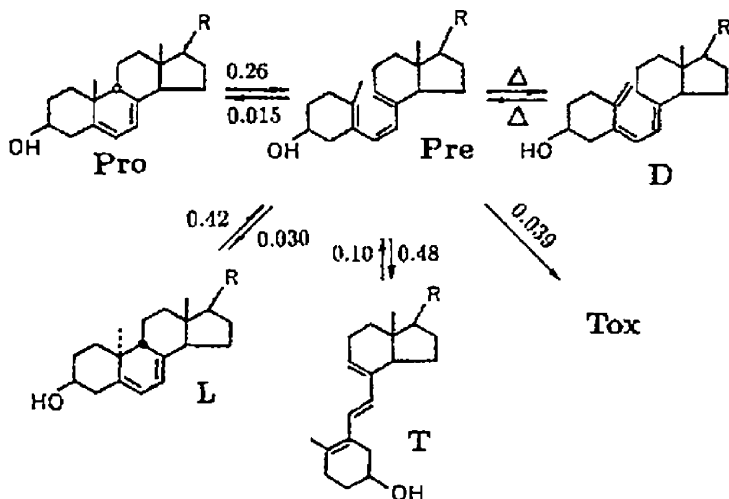
Our next idea was to add provitamin D to a cholesteric mixture already possessing its pitch in the visible range [21]. Here we show a possibility to observe color changes (helical pitch variation) in induced cholesteric systems as a result of photoisomerization of provitamin D₂.

MATERIALS AND METHODS

The cholesteric mixture used should be composed of a nematic host and a chiral dopant, both transparent in visible and near-UV range and nonphotoisomerizable. As nematic hosts, we used PCH-5 (a phenylcyclohexane mixture, Merck) and a mixture of ZLI 1184 + ZLI 1185 (cyclohexanes, Merck).

¹The terminology “vitamin D” is employed here in the general sense, although two principal chemical species are available. Vitamins D₂, ergocalciferol (C₂₈H₄₄O), and D₃, or cholecalciferol; (C₂₇H₄₄O), are produced from their precursors ergosterol and 7-dehydrocholesterol (7-DHC), respectively.

²In different nematic LC matrices (ZLI-1695, ZhK-805) $\text{HTP} = 1.8 \div 1.9 \mu\text{m}^{-1}\text{mol.frac}^{-1}$ for provitamins D₂ and D₃, and $\text{HTP} = -5.4 \div 5.9 \mu\text{m}^{-1}\text{mol.frac}^{-1}$ for vitamin D₂.



SCHEME 1 The reaction scheme of vitamin D synthesis: **Pro**, provitamin D; **Pre**, previtamin D; **T**, tachysterol; **L**, lumisterol; **Tox**, toxysterols; **D**, vitamin D. R = C₉H₁₇ – Vitamin D₂ series, R = C₈H₁₇ – Vitamin D₃ series. Numbers with arrows represent the quantum yields [22,26].

As chiral dopants, we used left-handed Tigogenin (T), a natural steroid [25], and left-handed ZLI 811 (Merck). Ergosterol was used from Sigma.

The experimental studies were carried out using a standard sandwich-type cell (thickness ~10 μm). The transmission spectra measurements were made at room temperature using a Specord M40 spectrophotometer. A 100 W middle pressure mercury lamp was used for ultraviolet (UV) irradiation, and the shortest wavelengths (>280 nm) were removed by the filter.

The induced cholesteric liquid crystals used in our study have a broad temperature range of the mesophase. An important point is that helical pitch of the UV biosensor should be temperature independent (or weakly dependent).

RESULTS AND DISCUSSION

Depending on the handedness of the initial cholesteric structure, the pitch, after doping by ergosterol, can either increase or decrease. In our case, both chiral dopants were left-handed, and unwinding of the helical pitch was observed (Figures 1 and 2)³. Doping of 10% ergosterol into the

³The selective reflection band has a bell-like shape, and its central wavelength is denoted as “maximum selective reflection” in the Figures 1–4.

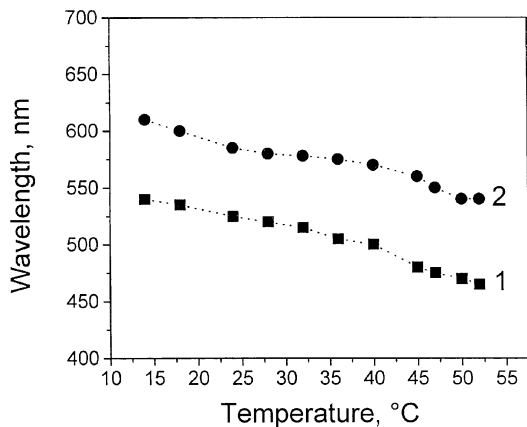


FIGURE 1 Wavelength of maximum selective reflection (helical pitch) as function of temperature for induced cholesteric mixtures. 1-80%PCH-5 + 20%T, 2-90% (80%PCH-5 + 20%T) + 10% provitamin D₂.

two-component cholesteric mixture (80%PCH-5 + 20%T) gave rise to the 70 nm long-wave shift of the selective reflection band (SRB: Figure 1). Doping of 8% ergosterol to the three-component cholesteric mixture [68% (50%ZLI-1184 + 50%ZLI-1185) + 32%ZLI-811] induced lesser long-wave shift (~ 40 nm) of the SRB (Figure 2).

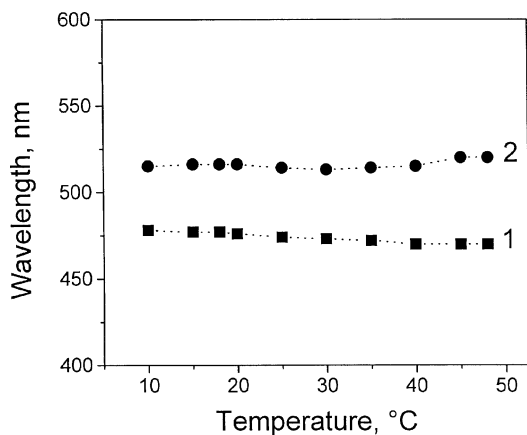


FIGURE 2 Wavelength of maximum selective reflection as function of temperature for the induced cholesteric mixtures. 1-68% (50%ZLI-1184 + 50%ZLI-1185) + 32%ZLI-811, 2-92%[68%(50%ZLI-1184 + 50%ZLI-1185) + 32%ZLI-811] + 8% provitamin D₂.

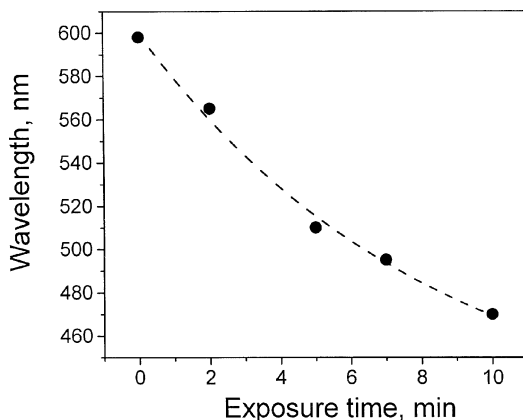


FIGURE 3 Dependence of the maximum of selective reflection wavelength on UV exposure time for 90% (80%PCH-5 + 20%T) + 10% provitamin D₂. Symbols, experimental data; dotted line, first order exponential decay fitting.

At the same time, the undesirable temperature shift of the SRB in case of the first mixture amounted to 70 nm (short-wave) as temperature changed from 14°C to 50°C (Figure 1), whereas rather high stability of SRB was observed for the second mixture (Figure 2).

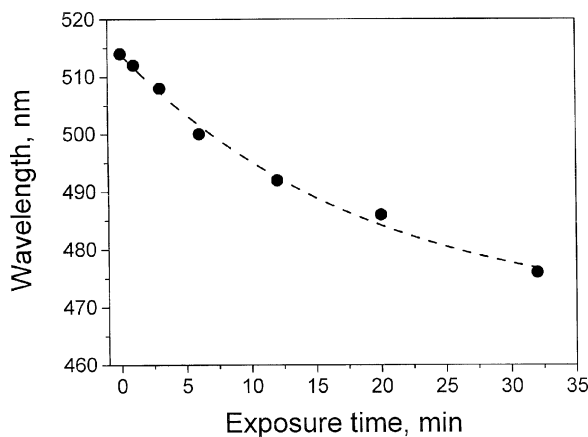


FIGURE 4 Dependence of the maximum selective reflection wavelength on UV exposure time for 92% [68% (50%ZLI-1184 + 50%ZLI-1185) + 32%ZLI-811] + 8% provitamin D₂. Symbols, experimental data; Dotted line, first order exponential decay fitting.

Under UV irradiation, as a result of phototransformation of ergosterol, the pitch changed in the opposite direction, i.e., back to the values for the initial (undoped) cholesteric structure and further on (Figures 3 and 4). This is in agreement with the data on the effective helical twisting sense of vitamin D₂, known to be opposite to that of ergosterol [24].

The values of the SRB changes with UV exposure (the color change) were different in case of two cholesteric matrices. In the 1st case pronounced color change (~ 130 nm shift) was observed as a result of 10 min exposure (Figure 3), but in the 2nd case less perceptible color change (~ 40 nm shift) was observed after 30 min exposure.

CONCLUSIONS

1. We have shown a possibility of UVB radiation (280–315 nm) detection by monitoring the helical pitch changes caused by the photoinduced transformation of provitamin D₂ to vitamin D₂ in the cholesteric matrix.
2. The developed cholesteric sensor material, comprising a nematic LC, a UV-insensitive chiral dopant, and 8–10% of ergosterol, displayed shifts of the selective reflection peaks by up to 130 nm after 10 min of UV irradiation, making possible both instrumental and visual (by color change) monitoring of UVB radiation.

These preliminary results are promising for development of personal UV biosensor with visual detection of the vitamin D synthetic capacity of sunlight (or artificial UV source). More detailed investigations directed to optimization of cholesteric composition are in progress.

REFERENCES

- [1] Chilaya, G. (2001). *Cholesteric Liquid Crystals: Optics, Electrooptics and Photooptics*. In: *Chirality in Liquid Crystals*, Kitzrow, H.-S. & Bahr, Ch. (Eds.), New York: Springer Verlag, series "Partially Ordered Systems," Chap. 6, pp. 159–185.
- [2] (a) Chilaya, G. S. (2000). *Crystallography Reports*, 45, 871–886.
(b) Chilaya, G. S. (2000). *Kristallografiya*, 45, 944–960.
- [3] Ikeda, T. (2003). *J. Mater. Chem.*, 13(9), 2037–2057.
- [4] Ichimura, K. (2000). *Chem. Rev.*, 100, 1847–1873.
- [5] Chilaya, G. (1981). *Rev. Phys. Appliq.*, 16, 193–208.
- [6] Chilaya, G. S. & Lisetski, L. N. (1981). *Sov. Phys. Usp.*, 24, 496–510.
- [7] Chilaya, G. S. & Lisetski, L. N. (1986). *Mol. Cryst. Liq. Cryst.*, 140, 243–286.
- [8] Sackman, E. (1971). *J. Am. Chem. Soc.*, 93, 7088–7090.
- [9] Vinogradov, V., Khizhniak, A., Kutulya, L., Reznikov, Yu., & Reshetnyak, V. (1990). *Mol. Cryst. Liq. Cryst.*, 192, 273–278.
- [10] Bobrowski, A. Yu., Boiko, N. I., & Shibaev, V. P. (1999). *Liq. Cryst.*, 26, 1749–1765.
- [11] Van de Witte, P., Brehmer, M., & Lub, J. (1999). *J. Mater. Chem.*, 9, 2087–2094.

- [12] Vicentini, F., Cho, J., & Chien, L.-C. (1998). *Liq. Cryst.*, *24*, 483–488.
- [13] Chanishvili, A., Chilaya, G., Petriashvili, G., & Sikharulidze, D. (2001). *Proc. Of 6th European Conference on Liquid Crystals*, Halle, Germany, abstracts # 2-P3.
- [14] Yamaguchi, T., Inagawa, T., Nakazumi, H., Irie, S., & Irie, M. (2000). *J. Mater. Chem.*, *11*, 2453–2458.
- [15] Lee, H.-K., Doi, K., Harada, M., Tsutsumi, O., Kanazawa, A., Shionio, T., & Ikeda, T. (2000). *J. Phys. Chem. B* *104*, 7023–7028.
- [16] Chanishvili, A., Chilaya, G., Petriashvili, G., & Sikharulidze, D. *Mol. Cryst. Liq. Cryst* (to be published).
- [17] Terenetskaya, I. & Gvozдовsky, I. (2001). *Mol. Cryst. Liq. Cryst.*, *368*, 551–558.
- [18] Terenetskaya, I. & Gvozдовsky, I. (2001). *SPIE Proc.*, *4425*, 183–188.
- [19] Gvozдовsky, I. & Terenetskaya I. (2002). In *Biologic Effects of Light 2001*, Holick, M. F. (Ed.) Boston: Kluwer Academic Publishers, pp. 341–353.
- [20] Aronishidze, M., Chanishvili, A., Chilaya, G., Petriashvili, G., Tavzarashvili, S., Lisetski, L., Gvozдовsky, I., & Terenetskaya, I. (2003). *Abstracts of 7th European Conference on Liquid Crystals*, Jaca, Spain, 6–11 April, O2.
- [21] Korzovska, O. V., Terenetskaya, I. P., & Lisetski, L. N. (2000). *Biophysical Bulletin (Proc. Kharkiv Univ., No.488)*, *1*, 71–74 (2000).
- [22] Jacobs, H. J. C. & Havinga, E. (1979). *Photochemistry of Vitamin D and its Isomers and of Simple Trienes*, In *Advances in Photochemistry*, Pitts, J. N. et al. (Eds.), (New York: Wiley) pp. 305–373.
- [23] Mayer A. C. & Norman, A. W. (1991). *Vitamin D*, In *Encyclopedia of Human Biology*, (New York: Academic Press) pp. 859–871.
- [24] Gvozдовsky, I. & Terenetskaya, I. (2002). *Liq. Cryst. Today*, *11*, 8–12.
- [25] Chilaya, G. S., Elashvili, Z. M., Lisetski, L. N., Piliashvili, T. S., & Vinokur, K. D. (1981). *Mol. Cryst. Liq. Cryst.*, *74*, 261–273.
- [26] Abillon, E. & Mermet-Bouvier, R. (1973). *J. Pharm. Sci.*, *62*, 1688–1691.